sal+2 CH_3O]$^+$; 385.7 (11) [**2**−2 sal]$^{2+}$, 333.6 (100) [**2**−3 sal+ OH]$^{2+}$; IR (KBr): $\tilde{\nu}$ = 1645 (s, (C=O)), 1568 (m, br, (C=N)), 1352 (w, sal (C−O)), 1341 (w, L^{3-} (C-O)), 897 (w, sal), 762 cm^{-1} (w, sal); UV/Vis/NIR (acetonitrile): λ_{max} (ε) = 238 (72000), 327 (47000), 445 (sh), 602 nm (600); elemental analysis calcd for $C_{45}H_{54}N_6O_9Cu_3$ (%): C 53.32, H 5.37, N 8.29; found: C 52.98, H 5.22, N 8.23.

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[7] X-ray structure analysis data of **1**-$(BF_4)_3$·2 MeOH·$HNMe_2$·1.5 H_2O: formula $C_{58}H_{81}N_{13}O_{6.5}Cu_3B_3F_{12}$, M_r = 1515.41, black crystal 0.30 × 0.30 × 0.10 mm, a = 19.243(1), b = 16.521(1), c = 21.633(1) Å, β = 92.18(1)°, V = 6872.4(6) Å^3, ρ_{calcd} = 1.465 g cm^{-3}, μ = 10.10 cm^{-1}, empirical absorption correction by using SORTAV (0.751 ≤ T ≤ 0.906), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 23777 reflections collected (±h, ±k, ±l), ((sinθ)/λ) = 0.62 Å^{-1}, 13898 independent (R_{int} = 0.032) and 9859 observed reflections ($I \geq 2\sigma(I)$), 756 refined parameters, R = 0.087, wR^2 = 0.256, max. residual electron density 1.68 (−1.12) e Å^{-3}, close to the BF_4^-, refinement with split positions did not improve the model, therefore the anions were refined with isotropic thermal displacement parameters, the solvent molecules (2 methanol, 1 dimethylamine, and 1.5 water) were refined with one common isotropic thermal parameter each, hydrogen atoms on the nitrogen atom of the dimethylamine and at the water molecules not localized, other calculated and refined as riding atoms. X-ray structure analysis data of **3**: formula $C_{34}H_{52}N_2O_3Cu$, M_r = 600.32, green-yellow crystal 0.25 × 0.15 × 0.03 mm, a = 9.382(1), b = 13.052(1), c = 13.789(1) Å, α = 87.25(1), β = 86.88(1), γ = 87.79(1)°, V = 1683.0(3) Å^3, ρ_{calcd} = 1.185 g cm^{-3}, μ = 6.82 cm^{-1}, empirical absorption correction by using SORTAV (0.848 ≤ T ≤ 0.980), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 10380 reflections collected (±h, ±k, ±l), ((sinθ)/λ) = 0.62 Å^{-1}, 6793 independent (R_{int} = 0.052) and 5042 observed reflections ($I \geq 2\sigma(I)$), 375 refined parameters, R = 0.064, wR^2 = 0.142, max. residual electron density 0.98 (−0.54) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. For data collection and programs used see H. P. Wu, R. Aumann, R. Fröhlich, E. Wegelius, *Eur. J. Org. Chem.* **2002**, 361 – 368. CCDC-181141 (**1**-$(BF_4)_3$·2 MeOH·$HNMe_2$·1.5 H_2O) and CCDC-181142 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

Supramolecular Engineering with Macromolecules: An Alternative Concept for Block Copolymers**

Bas G. G. Lohmeijer and Ulrich S. Schubert*

Block copolymers represent an important class of materials, which have received widespread attention because of their remarkable micro- and nanophase morphology. This morphology leads to unique properties compared to homopolymers or their blends. Classical examples of block-copolymer morphology are lamellae, hexagonal-packed cylinders and body-centered-cubic arrays of spheres.[1] During the last decades, important advances have been made in the synthesis, characterization, and application of block copolymers. In particular, anionic polymerization has been successfully applied in their controlled synthesis.[2] Several other routes have been realized as well, for example, controlled radical polymerization,[3] cationic polymerization,[4] group transfer,[5] and metathesis,[6] or combinations of such techniques. Nevertheless, block-copolymer synthesis remains a challenge for certain materials and several interesting combinations could not be realized to date. On the other hand, recent developments in the field of supramolecular chemistry have shown that small (self-)complementary building blocks can lead, through self-organization processes, to large, well-defined structures, which are held together by noncovalent interactions such as hydrogen bonds[7] and metal-to-ligand coordination.[8] Herein we present a new highly controlled and well-defined construction principle for block copolymers that utilize supramolecular interactions, in this case metal-to-ligand coordination. By this method new combinations of block copolymers can be prepared, which are not accessible, or have been very difficult to access to date. This allows a comparison of the new metallo-supramolecular compounds with classical well-documented covalent block copolymers. For this purpose we chose the terpyridine ligand as the central building unit, which is well-known for its outstanding ability to form stable bis complexes with a large variety of transition-metal ions (Figure 1).[9] The main advantage of having a metal complex as the bridging unit is the possibility of cleavage at this junction point. Therefore new "smart materials" are accessible. Moreover, the metal ion being at the interface between the blocks may cause additional interesting features regarding morphology, thermal and mechanical as well as photophysical properties.

The construction of the supramolecular block copolymers works along the same principle as their covalent counterparts.

[*] Prof. Dr. U. S. Schubert, Ir. B. G. G. Lohmeijer
Laboratory of Macromolecular Chemistry and Nanoscience
Eindhoven University of Technology, P.O. Box 513
5600 MB Eindhoven (The Netherlands)
Fax: (+31) 40-247-4186
E-mail: u.s.schubert@tue.nl
and
Center for Nanoscience, Ludwig-Maximilians-Universität München
Geschwister-Scholl-Platz 1, 80539 München (Germany)

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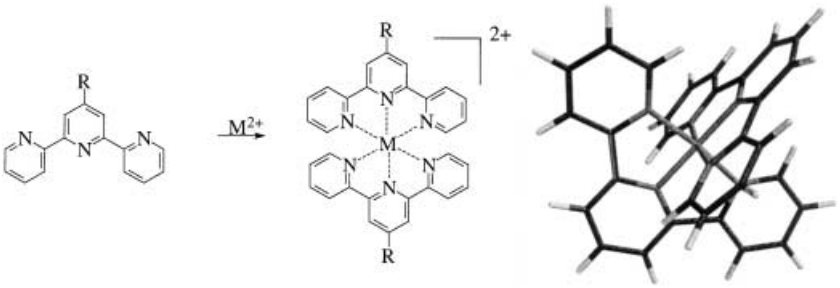


Figure 1. Bis(terpyridine) metal complex (left: schematic representation, right: results of the molecular modeling study).

First, defined oligomers of narrow polydispersities (< 1.15) and with functional end groups (telomers) are formed by controlled polymerization methods. The terpyridine ligand is introduced at the chain end(s) of the telomers by simple organic reactions. Combining the different terpyridine-functionalized oligomers by self-organization processes directly leads to the desired block copolymers (Figure 2). An extremely powerful tool in the construction of well-defined supramolecular block copolymers is the ability of the terpyridine ligand to bind selectively only to a single transition-metal ion and form a "mono"-complex under specific conditions (1:1 ratio of ligand:metal ion).[10] In particular, ruthenium ions have been used successfully in supramolecular chemistry to build up asymmetric complexes (Figure 2).[11]

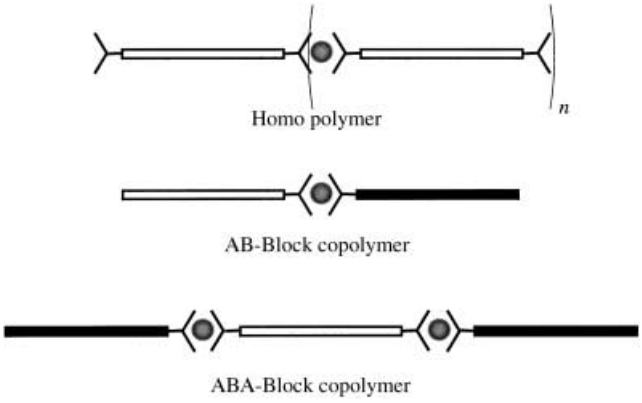
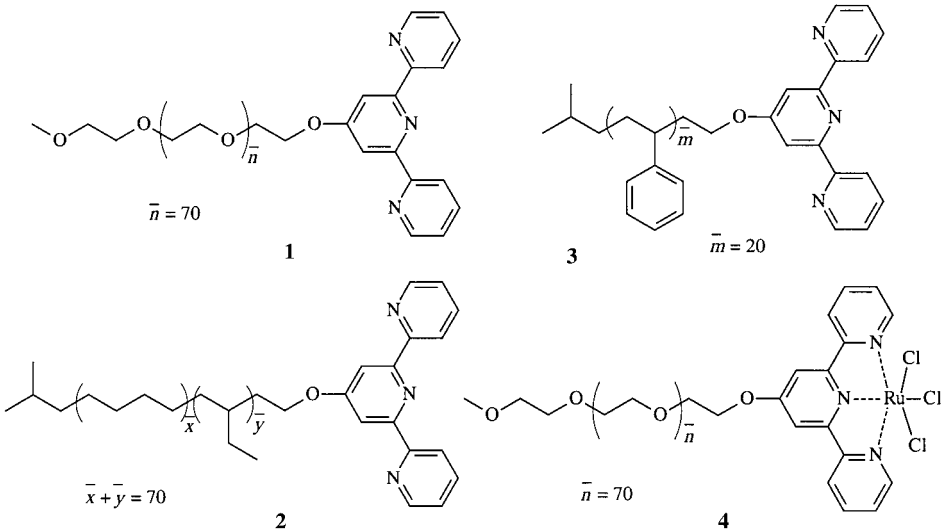


Figure 2. Modular engineering of A_n, AB-, and ABA-metallo-supramolecular block copolymers.

Herein we have used terpyridine-terminated polymers to engineer supramolecular AB, $(AB)_n$, and ABA block copolymers. To show the feasibility of this concept we chose well-known systems which also have covalent counterparts. Recently we demonstrated that the terpyridine ligand could be successfully introduced into hydroxy-functionalized oligomers of poly(ethyleneoxide) (PEO) and poly(tetramethyleneoxide) (PTMO) in a suspension of KOH in DMSO.[12] This strategy has now been extended to hydroxy-terminated polystyrene (PS)[13] and poly(ethylene-*co*-butylene) (PEB; Scheme 1), by utilizing toluene as the solvent and using a crown ether to improve the base solubility. The terpyridine ligand could react in high yields through a Williamson type ether formation reaction. For this purpose, different reaction conditions were optimized for each class of polymers. The complete derivatization of the prepolymers with terpyridine-moieties was demonstrated by ^{1}H NMR, ^{13}C NMR, UV/Vis, gel-permeation chromotography (GPC) and MALDI-TOF MS. To form AB-type polymer structures selectively, the poly(ethylenoxide) **1** was treated with $Ru(III)Cl_3$, which resulted exclusively in the desired monocomplex **4** (simply isolated by precipitation). This compound was then further treated, in a self-organization step, with the terpyridine-functionalized polymers **1**, **2**, and **3**, respectively. In this approach, ethanol is utilized as the reducing agent and *N*-ethylmorpholine as the catalyst, to reduce the Ru^{III} ions to Ru^{II} ions. Subsequently, a bis complex was formed between the ruthenium-filled terpyridine unit and the uncomplexed terpyridine unit, which resulted in unsymmetrical dimers. After exchange of the counterions by addition of an excess of NH_4PF_6, the supramolecular AB block copolymers **5**, **6**, and **7** were isolated by precipitation or extraction (Scheme 2). As an additional purification step, size-exclusion chromatography (BioBeads SX-1 in CH_2Cl_2) was applied. The low yields (35–50 %) could be explained by the extensive purification procedures in conjunction with the small amounts we were working with to date. The corresponding model complexes were isolated in yields up to 97 %.[9b] Low selectivity was not an issue, because homopolymers (AA or BB) could not be isolated.

Characterization by UV/Vis spectroscopy revealed the characteristic metal–ligand charge-transfer (MLCT) band of the bis(terpyridine) ruthenium(II) complex at 490 nm, while



Scheme 1. Terpyridine-functionalized building blocks, poly(ethyleneoxide) **1**, poly(ethylene-*co*-butylene) **2**, polystyrene **3**, and poly(ethyleneoxide) treated with the $Ru^{III}Cl_3$ compound **4**.

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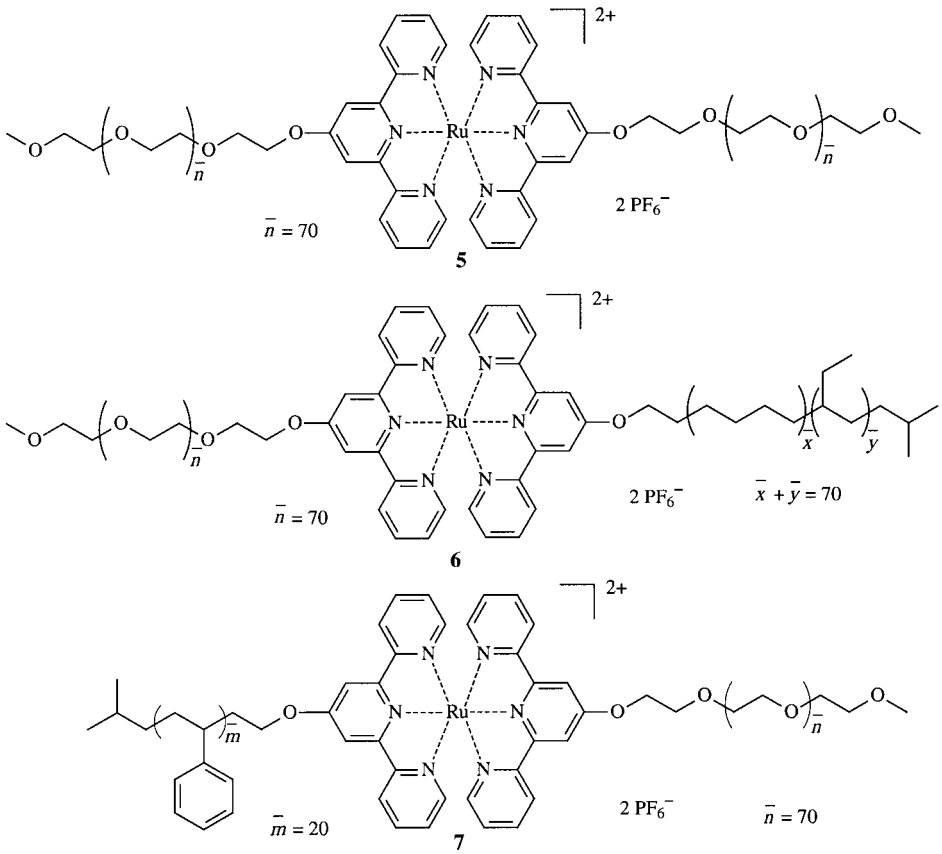

Scheme 2. Isolated metallo-supramolecular block copolymers: PEO_{70}-[Ru]-PEO_{70} (**5**), PEO_{70}-[Ru]-PEB_{70} (**6**), and PS_{20}-[Ru]-PEO_{70} (**7**).

the band at 390 nm—indicative of the mono(terpyridine) ruthenium(III) complex—has completely disappeared (Figure 3). This result is already unambiguous evidence for the successful formation of the block copolymers. In addition, because of the complexation of the ruthenium(II) ions, the signals arising from the terpyridine unit in both the ^1H and ^{13}C NMR spectra have shifted when compared to the uncomplexed terpyridine-functionalized prepolymers. All signals can be assigned by a comparison with the corresponding low-molar-mass model complexes. The integral ratio of the two polymer blocks was in good agreement with the expected ratio in all three cases. Also, this finding excludes the existence of any "homodimers". MALDI-TOF MS revealed the presence of the different blocks in the supramolecular block copolymers, although the supramolecular connection seems to be partly broken during the MALDI process (as is known for this type of metal complex).

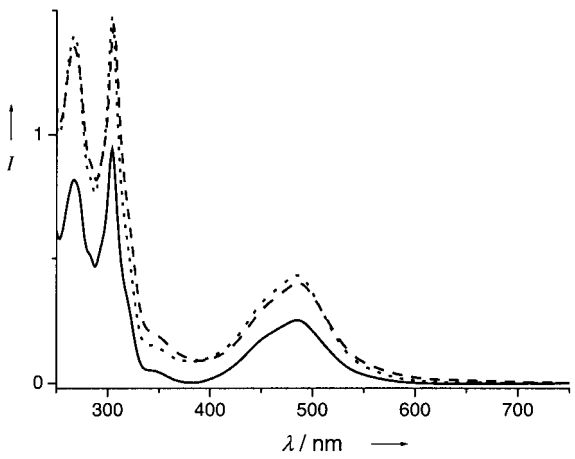

Figure 3. UV/Vis spectra of supramolecular block copolymers showing the metal-to-ligand charge-transfer band (MLCT) at 490 nm (in CH_3CN): —— **5**, – – – **6**, · · · · **7**.

Size-exclusion chromatography (GPC), which applied a UV/Vis as well as a refractive-index (RI) detector, revealed a single signal. This clearly shows that the metallo-supramolecular block copolymer was formed and that no homopolymers are present (Figure 4). The similar molar masses of **5**, **6**, and **7** result in a similar elution volume. The absence of further peaks also shows that the compounds are stable on the GPC column. Moreover, by varying the pH value from 0 to 14 in water, no changes in the UV/Vis spectrum could be observed, which indicates the unusual stability of the ruthenium complex. However, by utilizing redox processes or a large excess of a competitive chelator at higher temperatures (such as hydroxyethylethylenediaminotriacetic acid sodium salt, HEEDTA), the metal complex can be disassembled. Because the described A-[Ru]-B block copolymers represent amphiphilic materials, the formation of defined micelles is possible (see ref. [14] for the first examples). This oppportunity will certainly be of interest for applications in supported catalysis and nanotechnology.

In conclusion, we have demonstrated that a supramolecular approach towards block copolymers is feasible. In particular, combinations of blocks that to date have been inaccessible, or accessible by established routes only with great difficulties, can be engineered utilizing the described approach. By introducing the terpyridine ligand at the chain end(s) of different polymers of various lengths, a large number of building blocks for block copolymers can be obtained (several hundreds of potential functional prepolymers and telechelic molecules are already commercially available). Applying the strategy employed herein and using different metal centers and counterions, the possibilities for assembling supramolecular block copolymers of the type described are virtually unlimited. This approach is highly suitable for the development of libraries of block copolymers by combinatorial methods, which vary the block properties systematically. Initial experiments of this type are currently in progress. In

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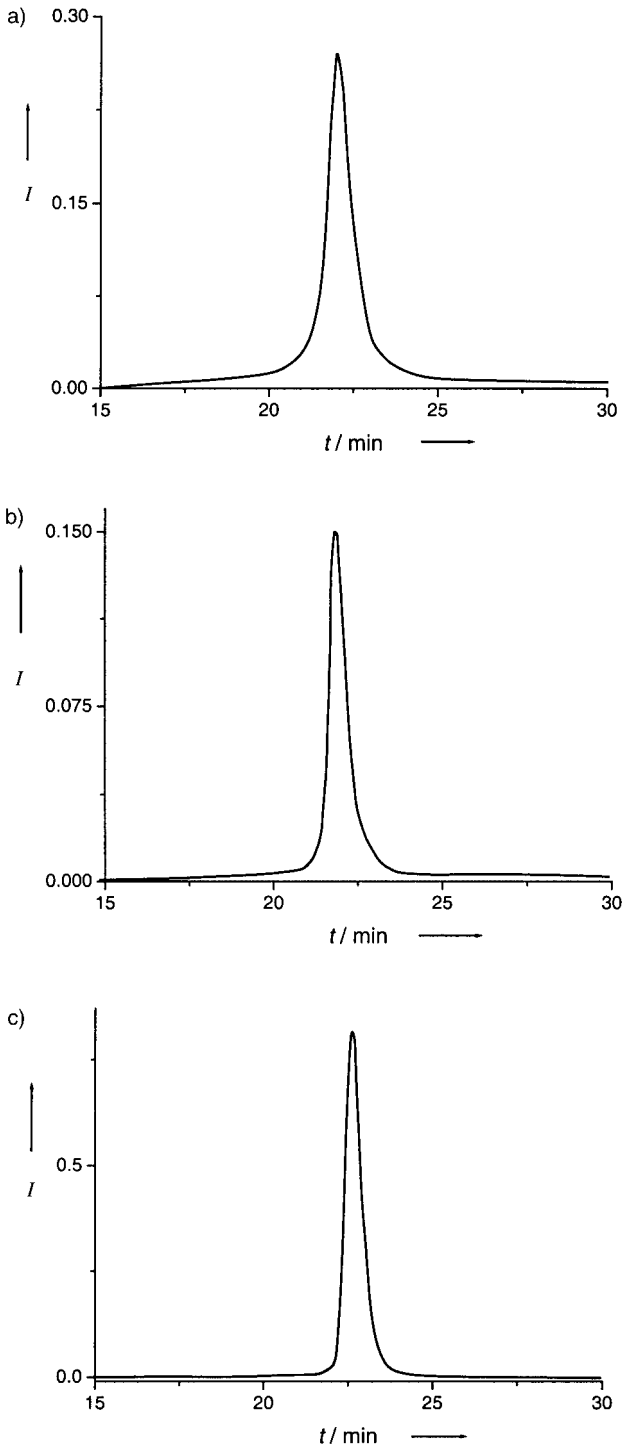

Figure 4. GPC traces of a) **5**, b) **6**, and c) **7** measured using a UV detector (eluant $CHCl_3$, polystyrene calibration standards).

addition, the reversibility of the supramolecular connections opens up avenues for the construction of "switchable" materials. This can lead to new applications, for example, as intelligent glues or release-on-demand systems.

Experimental Section

General preparation of **1**–**3**: Powdered KOH and the prepolymer (3:1 ratio) were stirred under Ar in dry DMSO at 70 °C or dry toluene with [18]-crown-6, heated under reflux. After 30 min, 4′-chloro-2,2′:6′,2″-terpyridine was added. The mixture was stirred for 24 h–48 h, then poured into cold water and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and the solvent removed in vacuo. All compounds were purified by preparative size-exclusion chromatography (BioBeads SX-1, CH_2Cl_2) and the compounds were subsequently precipitated by addition of a solvent in which they are insoluble. Compound **2** was further purified by column chromatography (silica, CH_2Cl_2 followed by CH_2Cl_2:Et_3N 9:1). Yields were 9.75 g of **1** (95 %), 3.9 g of **2** (46 %), and 2.10 g of **3** (75 %). Selected analytical data: **1**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.68$ (dt, $J = 4.8$, 2.0 Hz, 2H; H6, H6″), 8.61 (dt, $J = 8.0$, 2.0 Hz, 2H; H3, H3″), 8.04 (s, 2H; H3′, H5′), 7.85 (td, $J = 8.0$, 2.0 Hz, 2H; H4, H4″), 7.34 (ddd, $J = 8.0$, 4.8, 2.0 Hz 2H; H5, H5″), 4.40 (t, $J = 5.2$ Hz, 2H; tpyOCH_2), 3.93 (t, $J =$ 5.2 Hz, 2H; tpyO$CH_2C H_2$) 3.83–3.45 (m, 280H; PEO backbone), 3.38 ppm (s, 3H; OCH_3); UV/Vis (H_2O): $\lambda_{max} = 278$, 234 nm; MALDI-TOF MS: $M_n = 3436\ g\,mol^{-1}$; GPC (RI): $M_n = 2360$, polydispersity index (PDI) = 1.21. **2**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.69$ (dt, $J = 4.8$, 2.0 Hz, 2H; H6, H6″), 8.62 (dt, $J = 8.0$, 2.0 Hz, 2H; H3, H3″), 8.01 (s, 2H; H3′, H5′), 7.85 (td, $J = 8.0$, 2.0 Hz, 2H; H4, H4″), 7.32 (ddd, $J = 8.0$, 4.8, 2.0 Hz, 2H; H5, H5″), 4.25 (t, $J = 6.4$ Hz, 2H; tpyOCH_2), 1.58–0.68 ppm (m, 560H; PEB backbone); UV/Vis ($CHCl_3$): $\lambda_{max} = 278$, 243 nm; MALDI-TOF MS: $M_n = 4151\ g\,mol^{-1}$; GPC (UV): $M_n = 4450$, PDI = 1.19. **3**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): signals are broad $\delta = 8.67$ (bm, 2H; H6, H6″), 8.60 (bm, 2H; H3, H3″), 7.91 (s, 2H; H3′, H5′), 7.83 (bm, 2H; H4, H4″), 7.31–6.39 (bm, 102H; C_6H_5 PS backbone; H5, H5″), 4.11–3.96 (bm, 2H; tpyOCH_2), 2.66, 2.18–1.10, 0.78 ppm (bm, 49H; CH_2, CH PS backbone); UV/Vis ($CHCl_3$): $\lambda_{max} = 278$, 243 nm; MALDI-TOF MS: $M_n =$ $2104\ g\,mol^{-1}$; GPC (UV): $M_n = 1850$, PDI = 1.10.

Preparation of **4**: A solution of **2** (1.00 g, 0.29 mmol) in methanol (25 mL) was stirred at 60 °C. Then an equimolar amount of $RuCl_3 \cdot n\,H_2O$ (0.076 g, 0.29 mmol) was added. Stirring was continued overnight. Subsequently, the reaction mixture was cooled to −20 °C. The resulting dark orange precipitate was collected by filtration and washed twice with ice-cold water, followed by diethyl ether, yielding 1.05 g of product (99 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.92$–3.46 (m, 280H; PEO backbone), 3.38 ppm (s, 3H OCH_3); UV/Vis (H_2O): $\lambda_{max} = 272$, 375 nm; MALDI-TOF MS: $M_n = 3447\ g\,mol^{-1}$.

General procedure for the preparation of **5**–**7**: A solution of **1**, **2**, or **3** (1:1 ratio), respectively, and **4** in MeOH (5 mL) was stirred for 30 min, heating under reflux. A few drops of *N*-ethylmorpholine was added and the solution turned from orange to red. Heating under reflux was continued overnight, after which an excess of NH_4PF_6 (45 mg, 0.27 mmol) was added. The crude products were collected by filtration of the precipitate or extraction with CH_2Cl_2 after pouring them into water. Further purification was carried out by preparative size-exclusion chromatography (BioBeads SX-1, THF and/or CH_2Cl_2). Excess NH_4PF_6 was washed out with water by dissolving **5**, **6**, or **7** in $CHCl_3$. Yields were 97 mg of **5** (50 %), 76 mg of **6** (36 %), and 40 mg of **7** (35 %). Selected analytical data: **5**: ^{1}H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 8.49$ (dt, $J = 8.0$, 1.2 Hz, 4H; H3, H3″), 8.35 (s, 4H; H3′, H5′), 7.91 (td, $J = 8.0$, 1.2 Hz, 4H; H4, H4″), 7.37 (dt, $J = 5.6$, 1.2 Hz, 4H; H6, H6″) 7.16 (ddd, $J = 8.0$, 5.6, 1.2 Hz, 4H; H5, H5″), 4.67 (t, $J = 4.4$ Hz, 4H; tpyOCH_2), 4.05 (t, $J = 4.4$ Hz, 4H; tpyOCH$_2C H_2$), 3.80–3.38 (m, 570H, PEO backbone), 3.31 ppm (s, 6H; OCH_3); UV/Vis (CH_3CN): λ_{max}: 486, 304, 267 nm; GPC (UV): $M_n = 16780$, PDI = 1.13; MALDI-TOF MS: $M_n = 6627\ g\,mol^{-1}$. **6**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.40$ (dt, $J = 7.2$, 1.2 Hz, 2H; H3, H3″ PEO), 8.36 (dt, $J = 8.0$, 1.2 Hz, 2H; H3, H3″, PEB), 8.29 (s, 2H; H3′, H5′, PEO), 8.17 (s, 2H; H3′, H5′, PEB), 7.81 (m, 4H; H4, H4″, PEB + PEO), 7.37 (m, 4H; H6, H6″, PEB + PEO), 7.18 (m, 4H; H5, H5″, PEB + PEO), 4.76 (t, $J = 4.0$ Hz, 2H; tpyOCH_2, PEO), 4.58 (t, $J = 4.8$ Hz, 2H; tpyOCH_2, PEB), 4.09 (t, $J =$ 4.0 Hz, 2H; tpyOCH$_2C H_2$, PEO), 3.87–3.41 (m, 290H, PEO backbone), 3.38 (s, 3H; OCH_3), 1.68–0.80 ppm (m, 580H, PEB backbone); UV/Vis (CH_3CN) λ_{max}: 486, 304, 267 nm; GPC (UV): $M_n = 12410$, PDI = 1.10; MALDI-TOF MS: $M_n = 7502\ g\,mol^{-1}$. **7**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.36$ (td, $J = 8.0$, 1.2 Hz, 2H; H3, H3″, PEO), 8.26 (s, 2H; H3′, H5′, PS), 8.17 (bm, 2H; H3, H3″, PS), 7.88–7.73 (bm, 6H; H3, H3″(PS), H3′, H5′ (PS), H4, H4″ (PEO)), 7.33–6.32 (m, 110H; C_6H_5 PS backbone and tpy signals), 4.74 (t, $J = 3.6$ Hz, 2H; tpyOCH_2, PEO), 4.28–4.04 (m, 4H, tpyOCH$_2C H_2$ (PEO), tpyOCH_2 (PS)), 3.92–3.42 (m, 290H; PEO backbone), 3.38 (s, 3H; OCH_3), 1.72–0.60 ppm (m, 50H; CH_2, CH PS

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backbone); UV/Vis (CH_3CN): λ_{max}: 486, 305, 268 nm; GPC (UV): M_n = 7800, PDI = 1.08; MALDI-TOF MS: M_n = 5348 g mol^{-1}.

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Unusual P=C Bond Cleavage by Double Dichlorosilylene Transfer from Trichlorosilyltrimethylgermane to *P*-Phosphanyl Phosphaalkenes

Wolf-Walther du Mont,* Thorsten Gust, Emma Seppälä, Cathleen Wismach, Peter G. Jones, Ludger Ernst, Jörg Grunenberg, and Heinrich C. Marsmann

Dedicated to Professor Hans Bürger on the occasion of his 65th birthday

The major breakthroughs in the chemistry of stable carbenes and Group 14 carbene analogues in the last two decades were based on the use of sterically and electronically stabilizing substituents.[1] Concerning short-lived dihalogenosilylenes, however, very little synthetic progress has been made even 30 years after the basic high-temperature and matrix studies of Timms et al.[2,3] Oligomeric silanes of the empirical formula $SiCl_2$ are synthetically available, but they do not behave as sources of monomeric $SiCl_2$;[4] the alternative use of Si_2Cl_6[5] or $HSiCl_3$[6] as precursors is very limited. Herein, we report the use of trichlorosilyltrimethylgermane ($Me_3GeSiCl_3$, **1**)[7,8] as a new reagent for the transfer of $SiCl_2$ moieties to *P*-phosphanyl phosphaalkenes under very mild reaction conditions.

Pure **1**—a monomeric molecular compound in the gas phase—[7c] is thermally stable; in the presence of tertiary amines and phosphanes, however, **1** partially decomposes to $(Me_3Ge)_2Si(SiCl_3)_2$, Me_3GeCl, and $SiCl_4$; this observation was explained by sequences of nucleophile-catalyzed transfers of Me_3Ge and $SiCl_3$.[7,8] Alternatively, for the $SiCl_3$ transfer, the formation of $(Me_3Ge)_2Si(SiCl_3)_2$ may imply insertion reactions of nucleophile-coordinated dichlorosilylene ($SiCl_2$) into Si–Cl bonds.[7,8] If nucleophiles such as Et_3N and iPr_3P can really induce the α-elimination of chlorogermanes from **1** [Eq. (1)],[9] then trichlorosilylgermanes, such as **1**, would be important reagents for $SiCl_2$ transfer reactions.

Our first choice as $SiCl_2$ trapping reagents were the *P*-phosphanyl phosphaalkenes $(Me_3Si)_2C{=}P\text{-}PRR'$(**2a**: R, R′ = *i*Pr; **2b**: R = *t*Bu, R′ = *i*Pr).[10] The dialkylphosphanyl groups within the reagent were intended to induce the desired α elimination at **1** [Eq. (1)] and coordinate intermediate $SiCl_2$, the adjacent P–P bonds may allow subsequent $SiCl_2$ insertion reactions, and the P=C bonds should be suitable for [2+1] cycloadditions with silylenes, similar to the known reactions of

[*] Prof. Dr. W.-W. du Mont, Dipl.-Chem. T. Gust, M. Sc. E. Seppälä, Dipl.-Chem. C. Wismach, Prof. Dr. P. G. Jones, Prof. Dr. L. Ernst
Institut für Anorganische und Analytische Chemie
Technische Universität Braunschweig
Postfach 3329, 38023 Braunschweig (Germany)
Fax: (+49) 531-3915387
E-mail: w.du-mont@tu-bs.de

Dr. J. Grunenberg
Institut für Organische Chemie der Technischen Universität Braunschweig (Germany)

Prof. Dr. H. C. Marsmann
Anorganische und Analytische Chemie
Universität-Gesamthochschule Paderborn
Warburger Strasse 100, 33098 Paderborn (Germany)

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